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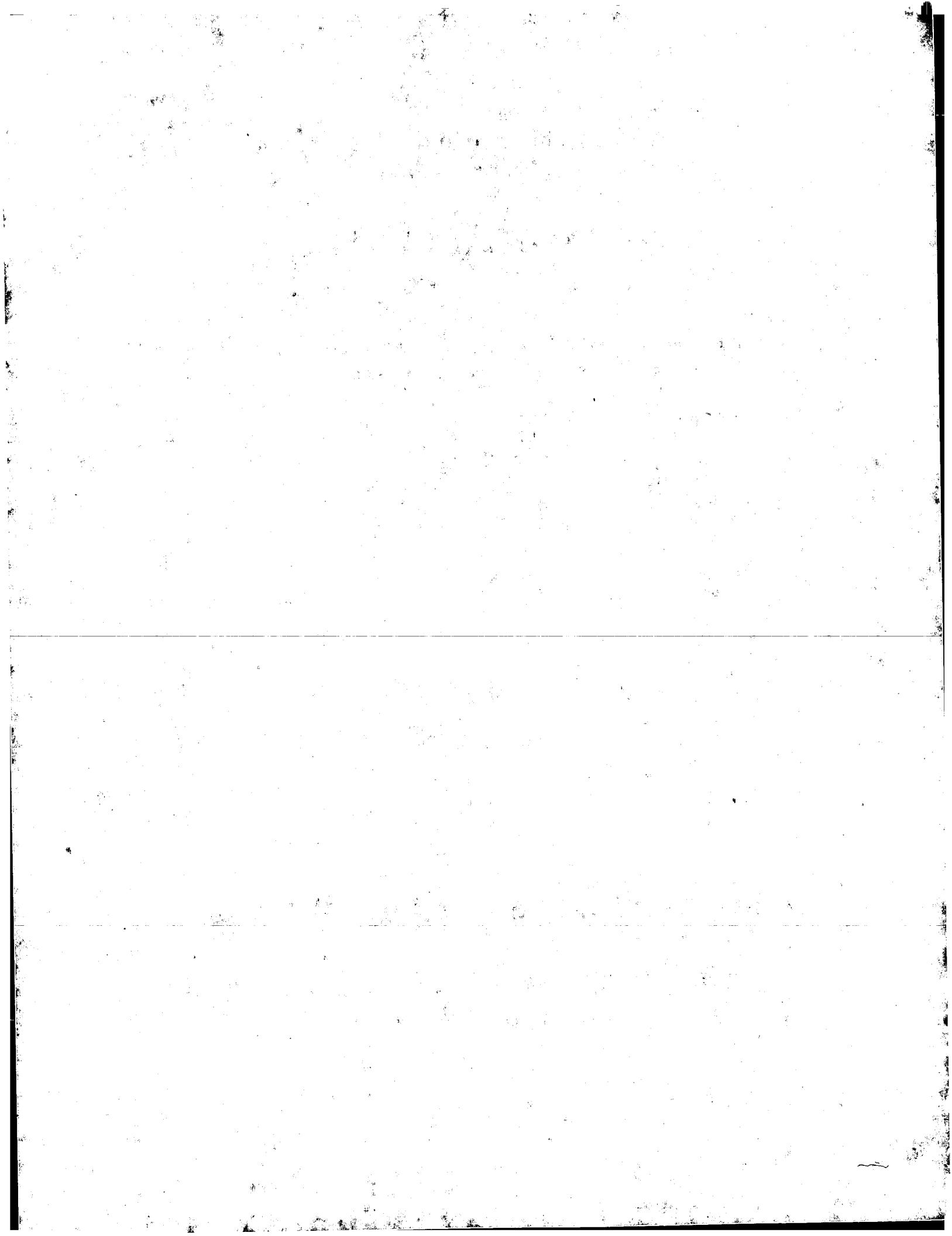
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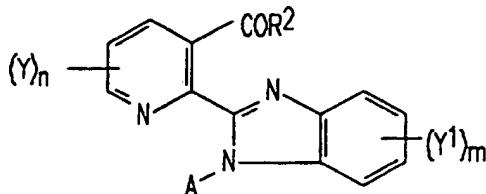
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(54) New herbicidal compositions.

(57) Benzimidazoyl derivatives of formula



wherein Y represents an optionally substituted alkyl, alkenyl, alkynyl or cycloalkyl group; or a group -OR, -SR, -SO₂R³, halogen, O-aryl, cyano, -NR⁴R⁵, aryl, aralkyl or nitro;

R² represents a group -OH, -NR⁴R⁸ or -XM; A represents -SO₂B;

Y¹ represents an optionally substituted alkyl, alkenyl or alkynyl group; or an optionally substituted cycloalkyl group; or a group such as -SR, -OR, -OR^{1a}, halogen, aryl, aralkyl, -Oaryl or -NR⁷R⁸;

n is zero or an integer from 1 to 3; m represents an integer from 1 to 4;

R represents an optionally substituted alkyl or cycloalkyl group;

R^{1a} represents an optionally substituted alkenyl or alkynyl group;

R⁷ and R⁸ represent independently a group such as hydrogen, R, aryl or aralkyl; X represents oxygen or sulphur;

M represents optionally substituted alkyl, optionally substituted cycloalkyl, or an aryl, aralkyl, alkenyl, alkynyl, or an imine group;

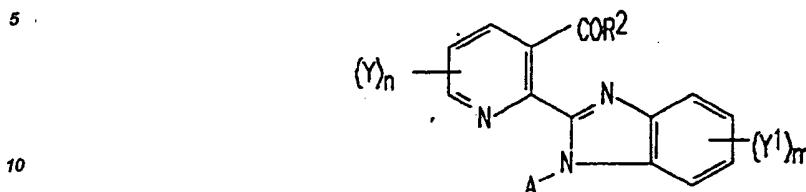
B represents optionally substituted alkyl group, optionally substituted cycloalkyl, aryl, aralkyl or NR⁷R⁸;

and agriculturally acceptable salts thereof;
herbicidal compositions comprising these compounds and their application to crop protection.

EP 0 509 717 A2

This invention relates to novel compounds, processes for their preparation, compositions containing them and their uses as herbicides.

The present invention provides benzimidazolyl derivatives of general formula I:-



15 wherein

Y represents:

a straight- or branched- chain alkyl, alkenyl or alkynyl group containing up to eight carbon atoms optionally substituted by one or more groups R¹, which may be the same or different; or

20 a group selected from -OR, -SR, -SO₂R³, halogen, O-aryl, cyano, -NR⁴R⁵, aryl, aralkyl, nitro, or a cycloalkyl group containing from 3 to 6 carbon atoms optionally substituted by one or more R¹ groups which may be the same or different;

Y¹ represents:-

25 a straight- or branched- chain alkyl, alkenyl or alkynyl group containing up to eight carbon atoms which is optionally substituted by one or more R¹ groups which may be the same or different; or a cycloalkyl group containing from 3 to 6 carbon atoms optionally substituted by one or more R¹ groups which may be the same or different; or

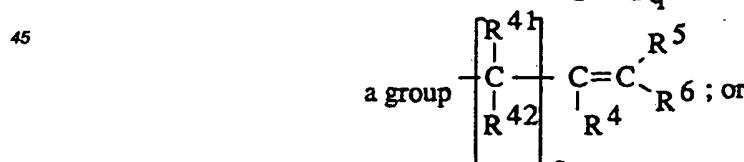
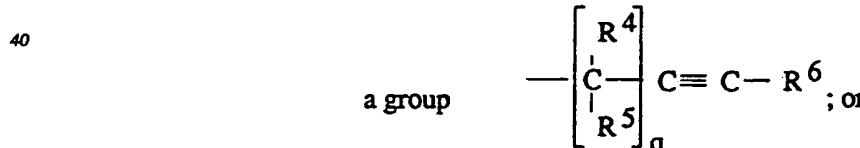
a group selected from -SR, -OR, -OR^{1a}, halogen, aryl, aralkyl, O-aryl or -NR⁷R⁸;

R² represents:-

30 a group -OH or -NR⁷R⁸;
or -X-M, where X represents oxygen or sulphur, and

M represents:-

35 a straight- or branched- chain alkyl group containing up to eight carbon atoms optionally substituted by one or more R¹ groups which may be the same or different; or a cycloalkyl group containing from 3 to 6 carbon atoms optionally substituted by one or more R¹ groups which may be the same or different; or a group selected from aryl and aralkyl; or



55 A represents a group -SO₂B;

B represents:-

a straight- or branched- chain alkyl group containing up to 6 carbon atoms optionally substituted by one or more groups, which may be the same or different, selected from -OR³, -SR³ and halogen; or

a cycloalkyl group containing from 3 to 8 carbon atoms optionally substituted by one or more groups, which may be the same or different, selected from -OR³, -SR³, R³ and halogen; or

a group selected from aryl, aralkyl and -NR⁷R⁸;

R represents:-

5 a straight- or branched- chain alkyl group containing up to eight carbon atoms optionally substituted by one or more groups R¹ which may be the same or different; or

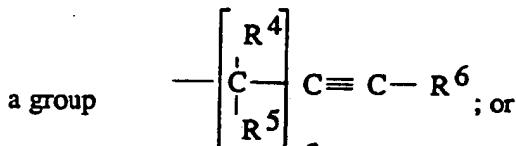
a cycloalkyl group containing from 3 to 6 carbon atoms optionally substituted by one or more groups R³ which may be the same or different;

R¹ represents:-

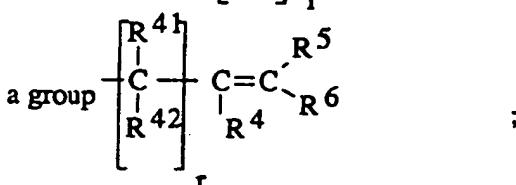
10 a cycloalkyl group containing from 3 to 6 carbon atoms; or
a group selected from -OR³, -SR³, halogen, R³ or O-aryl;

R^{1a} represents:-

15



20



25

R³ represents a straight- or branched- chain alkyl group containing up to 6 carbon atoms optionally substituted by one or more halogen atoms which may be the same or different;

30 R⁴, R⁴¹, R⁴² and R⁵, which may be the same or different, each represent hydrogen or a straight- or branched- chain alkyl group containing up to 6 carbon atoms optionally substituted by one or more halogen atoms which may be the same or different; or aryl;

R⁶ represents a group selected from R⁴ or aralkyl;

R⁷ and R⁸, which may be the same or different, each represent:-

35 a hydrogen atom, or

a group selected from R, -OR³, -SR³, halogen, R³ or O-aryl, aryl or aralkyl; or R⁷ and R⁸ may form together with the nitrogen to which they are attached a heterocycle containing from 3 to 6 carbon atoms in the ring and zero, 1 or 2 additional heteroatoms in the ring selected from nitrogen, oxygen and sulphur;

R⁹ and R¹⁰, which may be the same or different, each represent:-

40 a hydrogen atom, or

a straight- or branched- chain alkyl group containing up to eight carbon atoms optionally substituted by one or more groups, which may be the same or different, selected from halogen, -OR or -S(O)_sR, where s is zero, 1 or 2; or a phenyl group optionally substituted by from one to four groups, which may be the same or different, selected from nitro, R, -NR⁴R⁵, halogen or -S(O)_sR; or

45 a 5 or 6 membered heterocycle containing from 3 to 5 carbon atoms in the ring and one or more heteroatoms in the ring selected from nitrogen, sulphur or oxygen, e.g. thienyl, furyl, piperidyl, thiazolyl, optionally substituted by one or more groups R¹ which may be the same or different;

or R⁹ and R¹⁰ may form together with the nitrogen to which they are attached a heterocycle containing 4 or 5 carbon atoms in the ring, which may be optionally substituted by from 1 to 3 groups R³ which may be the same or different;

50 'aryl' represents:-

a phenyl group optionally substituted by from 1 to 4 groups which may be the same or different selected from -OR³, -SR³, halogen or R³; or

a 5 or 6 membered heterocycle containing from 3 to 5 carbon atoms in the ring and one or more

55 heteroatoms in the ring selected from nitrogen, sulphur or oxygen, e.g. thiophenyl, furyl, piperidyl, thiazolyl; optionally substituted by one or more groups, which may be the same or different, selected from -OR³, -SR³, halogen or R³;

'aralkyl' represents a group -(CR⁴R⁵)_p-aryl (e.g. benzyl);

m represents an integer from 1 to 4, the groups Y¹ being the same or different when m is greater than 1;

n represents zero, or an integer from 1 to 3;

p represents one or two;

q represents an integer from one to three;

r represents an integer from one to five;

when r, p or q is greater than one, the groups -CR⁴R⁵- and the groups -CR⁴¹R⁴²- may be the same or different;

with the proviso that one of the groups Y¹ represents -OR^{1a}, in either the 4-position or the 5-position of the benzimidazole ring;

where n represents 2 or 3, two groups Y which are adjacent to each other in the 5- and 6- positions on the pyridine ring can, with the carbon atoms to which they attached, form a fused phenyl ring, or can form an aliphatic or aromatic ring having 5 or 6 atoms in the ring and having not more than 2 heteroatoms in the ring selected from oxygen and sulphur, e.g. thieno[2,3-b]pyridine, thieno[3,2-b]pyridine, furo[2,3-b]pyridine, furo[3,2-b]pyridine, 3,4-dihydropyran[3,2-b]pyridine, 2,3-dihydropyran[3,2-b]pyridine or 2,3-dihydropyran[3,2-b]pyridine;

and agriculturally acceptable salts thereof;

which possess valuable herbicidal properties.

Furthermore, in certain cases the substituents Y, Y¹, R² and A may give rise to optical isomerism and/or stereoisomerism. All such forms are embraced by the present invention.

By the term "agriculturally acceptable salts" is meant salts the cations or anions of which are known and accepted in the art for the formation of salts for agricultural or horticultural use. Preferably the salts are water-soluble.

Suitable salts formed by compounds of formula I which are acidic, i.e. compounds containing a carboxy group, with bases include alkali metal (e.g. sodium and potassium) salts, alkaline earth metal (e.g. calcium and magnesium) salts, ammonium and amine (e.g. diethanolamine, triethanolamine, octylamine, dioctylmethylamine and morpholine) salts.

Suitable acid addition salts, formed by compounds of general formula I containing an amino group, include salts with inorganic acids, for example hydrochlorides, sulphates, phosphates and nitrates and salts with organic acids, for example acetic acid. Preferred salts are those in which R² represents a group -XW, where W represents a cation selected from the alkali metals (e.g., Na, K, Li) or ammonium salts of formula -NR¹¹R¹²R¹³R¹⁴, where R¹¹, R¹², R¹³ and R¹⁴, which may be the same or different, each represent-

- a hydrogen atom, or
- a straight- or branched- chain alkyl group containing up to 6 carbon atoms optionally substituted by -OH; or aralkyl, not more than two of the radicals R¹¹ to R¹⁴ representing the aralkyl group;

It is to be understood that where reference is made in the present specification to the compounds of general formula I, such reference is intended to include salts where the context so permits.

Compounds of general formula (I) in which R² represents alkoxy, alkenyloxy or alkynyoxy are particularly used as intermediates in the preparation of other compounds of general formula (I).

A particularly important class of compounds because of their herbicidal properties are those in which:

- (a) A represents -SO₂NR⁷R⁸; and/or
- (b) R² represents -OH or -XM; and/or
- (c) Y represents an alkyl group containing one or two carbon atoms optionally substituted by one or more halogen atoms, for example methyl, ethyl or trifluoromethyl; and/or
- (d) Y¹ represents -OR, for example methoxy or ethoxy; or halogen, for example fluorine or chlorine; -OR^{1a} or -NR⁷R⁸; and/or
- (e) m represents one or two; and/or
- (f) R⁷ and R⁸, which may be the same or different, each represent a straight- or branched- chain alkyl group containing up to 4 carbon atoms optionally substituted by one or more atoms which may be the same or different selected from fluorine or chlorine; and/or
- (g) X represents oxygen; and/or
- (h) R⁴, R⁴¹, R⁴², R⁵ and R⁶, which may be the same or different, each represent hydrogen or a straight- or branched- chain alkyl group containing up to 4 carbon atoms optionally substituted by one or more halogen atoms; and/or
- (i) n represents zero, one or two; and/or
- (j) r represents one or two, most preferably one; the other symbols being as hereinbefore described.

A further preferred class of compounds of general formula (I) are those wherein:

B represents -SO₂NMe₂;

R² represents -OH or -X-M;

X represents oxygen;

M represents a methyl or 2-propynyl group, or a potassium or isopropylammonium cation;

Y¹ represents -OR^{1a} in the 4-position of the benzimidazole ring;

R^{1a} represents 2-propenyl, 2-propynyl or 2-butynyl;

Y represents methyl, ethyl, or two groups Y in the 5- and 6- positions of the pyridine ring together with the carbon atoms to which they are attached form a fused phenyl ring;

m represents one; and

n represents one or two.

Particularly important compounds because of their herbicidal properties include:-

1. 2-[1-(N,N-dimethylsulphamoyl)-4-(2-propenoxy)benzimidazol-2-yl]pyridine-3-carboxylic acid;
2. 2-[1-(N,N-dimethylsulphamoyl)-4-(2-propenoxy)benzimidazol-2-yl]-6-methylpyridine-3-carboxylic acid;
3. 2-[1-(N,N-dimethylsulphamoyl)-4-(2-propenoxy)benzimidazol-2-yl]-5-methylpyridine-3-carboxylic acid;
4. 2-[1-(N,N-dimethylsulphamoyl)-4-(2-propenoxy)benzimidazol-2-yl]-5-ethylpyridine-3-carboxylic acid;
5. 2-[1-(N,N-dimethylsulphamoyl)-4-(2-propenoxy)benzimidazol-2-yl]quinoline-3-carboxylic acid;
6. 2-[1-(N,N-dimethylsulphamoyl)-4-(2-propenoxy)benzimidazol-2-yl]pyridine-3-carboxylic acid;
7. 2-[1-(N,N-dimethylsulphamoyl)-4-(2-propenoxy)benzimidazol-2-yl]-6-methylpyridine-3-carboxylic acid;
8. 2-[1-(N,N-dimethylsulphamoyl)-4-(2-propenoxy)benzimidazol-2-yl]-5-methylpyridine-3-carboxylic acid;
9. 2-[1-(N,N-dimethylsulphamoyl)-4-(2-propenoxy)benzimidazol-2-yl]quinoline-3-carboxylic acid;
10. 2-[1-(N,N-dimethylsulphamoyl)-4-(2-propenoxy)benzimidazol-2-yl]-5-ethylpyridine-3-carboxylic acid;
11. 2-[1-(N,N-dimethylsulphamoyl)-4-(2-butynoxy)benzimidazol-2-yl]pyridine-3-carboxylic acid;
12. 2-[1-(N,N-dimethylsulphamoyl)-4-(2-butynoxy)benzimidazol-2-yl]quinoline-3-carboxylic acid;
13. 2-[1-(N,N-dimethylsulphamoyl)-5-(2-propynoxy)benzimidazol-2-yl]pyridine-3-carboxylic acid;
14. 2-propynyl 2-[1-(N,N-dimethylsulphamoyl)-4-(2-propynoxy)benzimidazol-2-yl]-5-methylpyridine-3-carboxylate;
15. isopropylammonium 2-[1-(N,N-dimethylsulphamoyl)-4-(2-propynoxy)benzimidazol-2-yl]pyridine-3-carboxylate; and
16. methyl 2-[1-(N,N-dimethylsulphamoyl)-4-(2-propynoxy)benzimidazol-2-yl]pyridine-3-carboxylate.

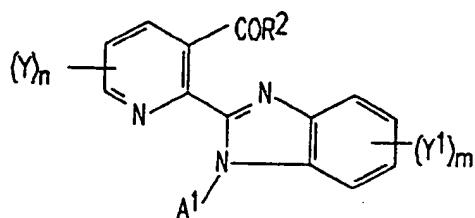
The numbers 1 to 16 are assigned to these compounds hereafter.

The compounds of general formula I can be prepared by the application or adaptation of known methods (i.e. methods heretofore used or described in the chemical literature), for example as hereinafter described. In the following description where symbols appearing in formulae are not specifically defined, it is to be understood that they are "as hereinbefore defined" in accordance with the first definition of each symbol in this specification.

It is to be understood that, in the description of the following processes, sequences may be performed in different orders and that suitable protecting groups may be required to achieve the compounds sought.

According to a feature of the present invention compounds of formula (I) in which A is the SO₂B group and R² is a -XM or -NR⁷R⁸ radical can be prepared by reacting a compound of the formula Cl-SO₂B with a compound of formula (Ia) :

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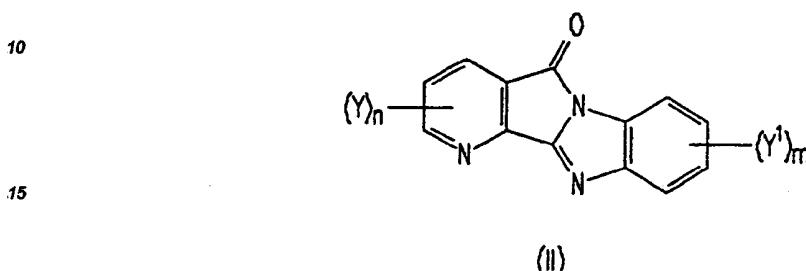
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in which A¹ is the hydrogen atom and R² is an -XM or -NR⁷R⁸ radical, in the presence of an acid acceptor such as potassium carbonat , triethylamin , 1,8-diazabicyclo[5.9.0]undec-7-en or sodium hydride, pref rably in an anhydrous medium using an aprotic polar solvent, for example , ethers (such as THF) or nitriles, at a temperature which is generally betw en 25°C and th reflux temp rature of th solv nt.

According to a further f atur of the pr sent invention compounds of formula (I) where R² is -XW in which X r presents oxyg n may be prepared from compounds of formula (I) where R² is -OH by reaction with th corresponding base.

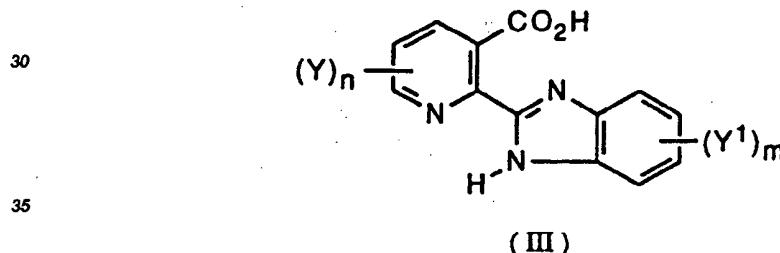
According to a further feature of the present invention compounds of the formula (I) in which R² represents -OH, may be prepared by the hydrolysis of compounds of formula (I) in which R² represents the group -XM using an inorganic base, for example lithium hydroxide, in a mixture of water and an alcohol, for example methanol, at a temperature between 0 °C and 25 °C.

5 Intermediates in the preparation of compounds of general formula I are prepared by the application or adaptation of known methods. Compounds of formula (Ia) in which A¹ is the hydrogen atom and R² is a radical -XM or -NR⁷R⁸ may be prepared by reacting a compound of formula (II) :



20 with an alkali metal alcoholate or alkaline earth metal alcoholate of the formula XM'M', wherein M' represents an alkali metal or alkaline earth metal cation, in an aprotic solvent and at a temperature between 0 °C and the boiling point of the solvent, or with an alcohol, thiol or oxime of the formula H-XM, or with an amine of the formula HNR⁷R⁸. The reaction with H-XM or HNR⁷R⁸ is generally performed in a polar organic solvent in the presence of an acid acceptor such as pyridine or triethylamine.

25 Compounds of formula (Ia) in which A¹ represents the hydrogen atom and R² is a radical -XM or -NR⁷R⁸ may be prepared by the reaction of the compound of formula (III) :



40 with an alcohol, thiol or oxime of formula H-XM or an amine of formula HNR⁷R⁸ in the presence of a coupling reagent, for example N,N-dicyclohexylcarbodiimide, in the presence of an inert solvent such as dichloromethane and at a temperature between 0°C and the reflux temperature of the solvent.

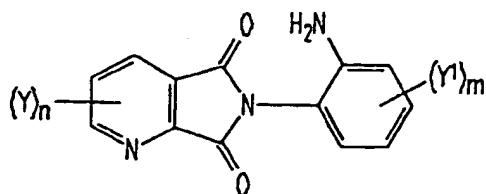
45 Compounds of formula (Ia) in which A¹ is the hydrogen atom and R² is a radical -XM in which X is the oxygen atom and M is as hereinbefore defined excluding the group -N=CR⁹R¹⁰, may be prepared by reacting a compound of formula (III) with a compound of formula H-OM in the presence of gaseous HCl with the compound of formula H-OM also acting as a solvent following a well known esterification process.

Compounds of the formula (Ia), where A¹ is the hydrogen atom and R² is the radical -XM, where X represents the oxygen atom and M is as hereinbefore defined excluding the group -N=CR⁹R¹⁰, may be prepared by heating a compound of formula (IIIa):

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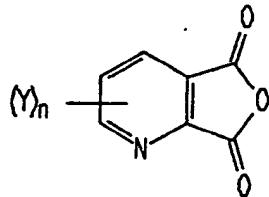
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(IIIa)

in a high boiling compound of formula H-OM, where M has the abovementioned meaning, for example ethoxyethanol at temperatures between 50 °C and the reflux temperature of the solvent.

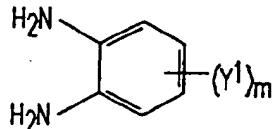
15 Compounds of formula (II) can be obtained by reacting an anhydride of formula (IV) with a 1,2-phenylenediamine of formula (V):

20



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(IV)



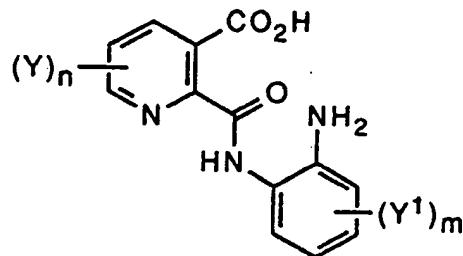
(V)

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by heating at temperatures between 110 and 190°C for between 1 and 3 hours, either in the absence of a solvent or in a solvent such as xylene, dichlorobenzene, or acetic acid, followed by the addition of acetic anhydride and heating at a temperature from 70°C to the boiling point of the solvent.

Compounds of formula (III) may be prepared by the cyclisation of the compounds of formula (VI):

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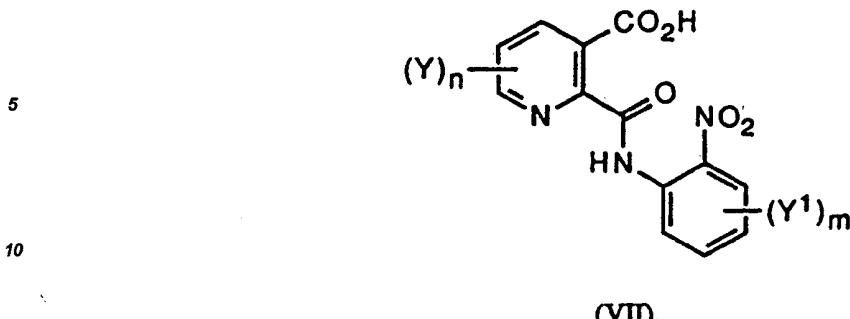


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(VI).

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The reaction may be carried out in an organic solvent such as ethoxyethanol under reflux. Compounds of formula (VI) may be obtained by the reaction of an anhydride of formula (IV) with a 1,2-phenylenediamine of formula (V) in an inert organic solvent, for example chloroform at temperatures between 0 °C and the boiling point of the solvent. Compounds of formula (VI) may also be obtained by reduction of compounds of formula (VII)



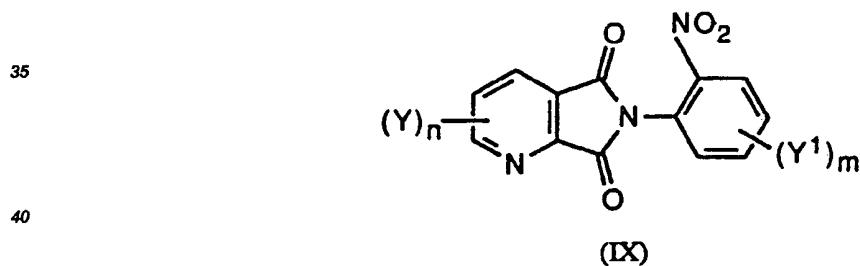
15 The reaction may be carried out in ethanol, in the presence of hydrogen chloride and of finely divided iron, at a temperature between 20 and 70°C.

Compounds of the formula (VII) may be obtained by the reaction of an anhydride of formula (IV) with a 2-nitroaniline of the formula (VIII):



in an organic solvent, for example chloroform or tetrahydrofuran, at a temperature between 20°C and the boiling point of the solvent.

30 Compounds of formula (IIIa) may be prepared by the reduction of a compound of formula (IX):

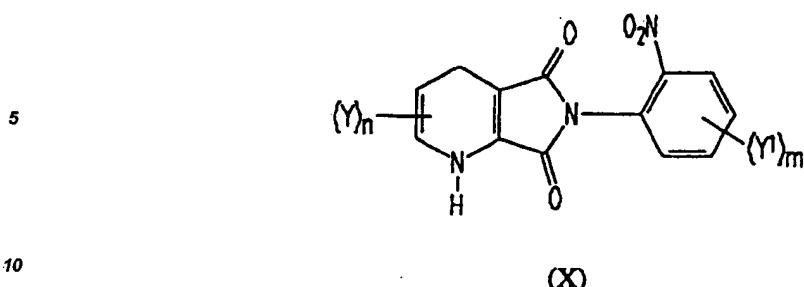


45 in ethanol in the presence of hydrogen chloride and of finely divided iron and at a temperature between 20 and 70 °C, or in an ethanol water mixture in the presence of sodium sulphide at a temperature between 20°C and the boiling point of the solvent mixture.

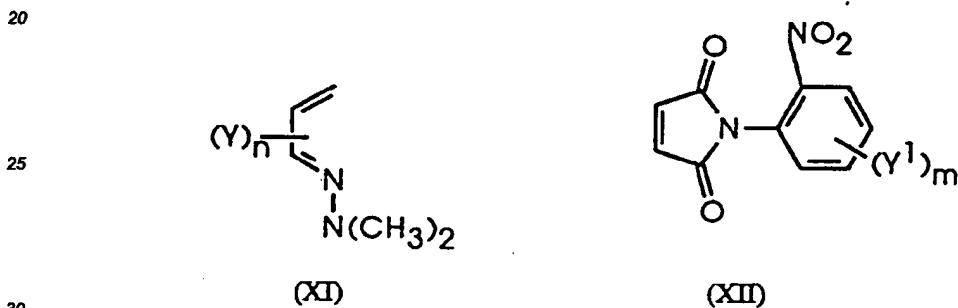
Compounds of formula (IX) in which n represents one may be prepared by the oxidation of a dihydropyridine of formula (X) :

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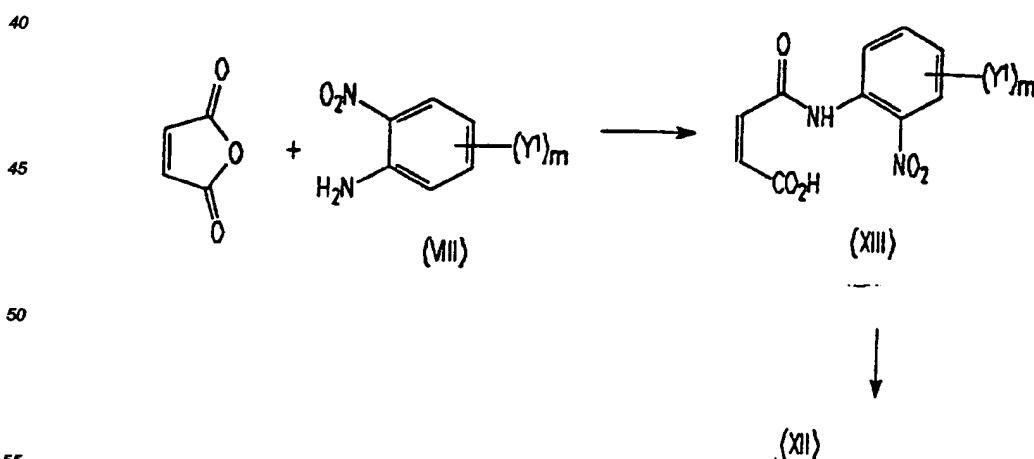


wherein n represents one, in the presence of an oxidising agent such as manganese(VI) oxide in an organic solvent such as acetic acid at a temperature between 20 and 80°C. Alternatively, oxidation can be accomplished by using sulphur in an inert hydrocarbon solvent, for example toluene at the reflux temperature of the solvent. Compounds of formula (X) in which n represents one can be obtained by the reaction between an azabutadiene of formula (XI), wherein n represents one, and a maleimide of formula (XII):



in a polar aprotic solvent, for example acetonitrile at a temperature between 0 and 40°C and subsequently treating the reaction mixture with silica gel.

The maleimide of formula (XII) may be prepared by the reaction of a 2-nitroaniline of formula (VIII) with maleic anhydride in an organic solvent, for example chloroform and at the reflux temperature of the solvent; followed by the cyclisation of the intermediate of formula (XIII) by heating in acetic acid at reflux temperature in the presence of sodium acetate:

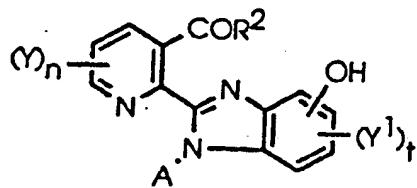


Azabutadienes of formula (XI) in which m or n presents one can be obtained as described by Waldner et al., Helvetica Chimica Acta, 1988, 71, 493.

According to a further feature of the present invention compounds of general formula (I) in which m or n is 1 or 2, one of the groups Y¹ represents a group -OR^{1a} which occupies the 4- or 5-position of the benzimidazole ring, R² represents a group -X-M where X is oxygen and M represents a straight- or branched-chain alkyl group containing up to 8 carbon atoms optionally substituted by one or more R¹ groups which may be the same or different, or a cycloalkyl group containing from 3 to 6 carbon atoms optionally substituted by one or more R¹ groups which may be the same or different and the group Y is as hereinbefore defined excluding an alkenyl or alkynyl group, chlorine, bromine or iodine, may be prepared by the reaction of a hydroxybenzimidazole of formula (XIV):

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(XIV)

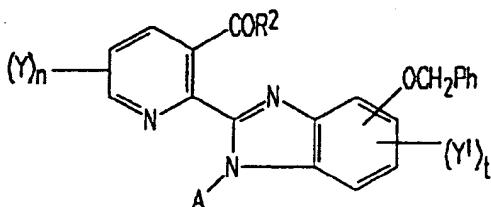
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wherein t is 0 or 1 and the hydroxy group occupies the 4- or 5-position of the benzimidazole ring, with a compound R^{1a}-L where L represents a leaving group, for example the tosyl group or a halogen atom (e.g. Cl, Br, I), to convert the hydroxy group in the 4- or 5-position of the benzimidazole ring into a group -OR^{1a}. The reaction is generally carried out in the presence of a base such as potassium carbonate in an inert organic solvent, for example acetone or DMF, at temperatures between 0°C and the reflux temperature of the solvent.

The compounds of formula (XIV) can be prepared by the hydrogenolysis of a benzyloxybenzimidazole of formula (XV):

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35



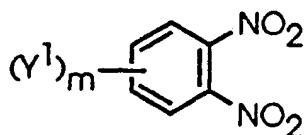
(XV)

40

wherein t represents zero or one, in a protic solvent such as methanol in the presence of hydrogen or a hydrogen donor such as 1,4-cyclohexadiene and of a hydrogenation catalyst for example palladium on charcoal. The reaction is generally carried out at room temperature and at atmospheric pressure. The compounds of formula (XV) can be prepared by the application of methods hereinbefore described.

The 1,2-phenylenediamines of general formula (V) may be obtained by the reduction of nitroanilines of formula (VIII) or of dinitrobenzenes of formula (XVI):

50



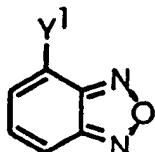
(XVI).

55

The reduction is carried out in a polar protic solvent, for example ethanol and water mixtures in the presence of sodium sulphide at a temperature between 20°C and the boiling point of the solvent, or in hydrochloric acid in the presence of stannous chloride at a temperature between 40 and 90°C.

Diamines of the formula (V) in which m represents 1 and Y¹ represents a group -OR^{1a} in the 3- position of the benzene ring, can be prepared by the reduction of a 2,1,3-benzoxadiazole of formula (XVII):

5



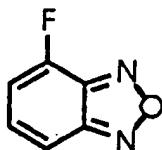
10

(XVII)

wherein Y¹ represents -OR^{1a}. The reduction can be carried out in an aqueous methanol mixture at reflux in the presence of hydrochloric acid and finely divided iron.

Compounds of the formula (XVII) in which Y¹ represents a group -OR^{1a} can be prepared by the reaction of 4-fluoro-2,1,3-benzoxadiazole as shown in formula (XVIII):

20



25

(XVIII)

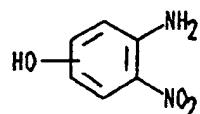
with an alcohol H-OR^{1a}. The reaction is typically carried out in acetone in the presence of a base such as potassium carbonate and at a temperature which is between 0°C and the reflux temperature of the solvent.

The conversion of a 4-fluoro-2,1,3-benzoxadiazole of formula (XVIII) into a compound of formula (XVII) in which Y¹ represents -OR^{1a} is conveniently carried out by reacting the former with an alcoholate M'-OR^{1a}, wherein M' represents an alkali metal cation (e.g. sodium or potassium), using the corresponding alcohol H-OR^{1a} as the reaction solvent, at a temperature between 20 °C and the boiling point of the alcohol.

4-Fluoro-2,1,3-benzoxadiazole, shown in formula (XVIII) can be prepared by the method described by L. Di Nunno et al. in Journal of the Chemical Society (C), 1433, 1970.

Nitroanilines of formula (VIII) where m represents 1 and Y¹ is the group -OR^{1a} may be prepared by the alkylation of an aminonitrophenol of formula (XIX):

40



45

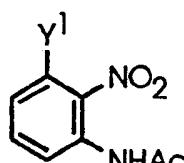
(XIX)

with an alkylating agent R^{1a}-halogen (where the halogen is for example chlorine bromine or iodine) in the presence of a base, for example potassium carbonate, in an inert solvent, for example acetone or DMF and at temperatures between 0°C and the reflux temperature of the solvent.

Nitroanilines of the formula (VIII) wherein m represents 1 and the group Y¹ occupies the 3- position of the benzene ring may be prepared by the hydrolysis of acetanilides of the formula (XX):

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10

The hydrolysis is generally carried out in an aqueous solution of sodium hydroxide in an alcoholic solvent such as ethanol at a temperature between 25 °C and the reflux temperature of the solvent.

15 Acetanilides of formula (XX) wherein Y¹ represents -OR¹a may be prepared by the displacement of the 3-nitro group in 2,3-dinitroacetanilide with an alcohol H-OR¹a. The reaction of 2,3-dinitroacetanilide with alcohols is usually accomplished by using the alcohol H-OR¹a as the solvent in the presence of at least one equivalent of the corresponding alcoholate Z-OR¹a wherein Z is selected from Na, K, Li, and at a temperature between 20°C and the boiling point of the alcohol.

20 2,3-Dinitroacetanilide may be prepared by using the method described by F.L.Greenwood et al., in Journal of Organic Chemistry, 797, 20, 1955.

25 2-Nitroanilines of general formula (VIII), dinitrobenzenes of formula (XIV) and anhydrides of formula (IV) are known or may be prepared by the application or adaption of known methods.

The compounds of formula (Ia) are novel and as such constitute a further feature of the invention.

The following Examples illustrate the preparation of compounds of general formula (I) and the Reference Examples illustrate the preparation of intermediates. Unless otherwise stated percentages are by weight.

25

EXAMPLE 1

Preparation of 2-[1-N,N-dimethylsulphamoyl-4-(2-propenoxy)benzimidazol-2-yl] piridine-3carboxylic acid, compound 1.

30

To a stirred suspension of methyl 2-[1-N,N-dimethylsulphamoyl-4-(2-propenoxy) benzimidazol-2-yl]pyridine-3-carboxylate (2.22g) in methanol (20ml) at room temperature was added a solution of lithium hydroxide (0.67g) in water. After stirring for 45 minutes the methanol was evaporated and the residue diluted with water and washed successively with ethyl acetate and diethyl ether. The aqueous solution was then acidified and the resulting gum extracted with ethyl acetate, dried and evaporated to give the title compound as a white solid, 2.1g, m.p. 80-83° C (Yield: 98%).

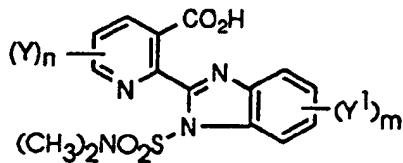
35 By proceeding in a similar manner the following compounds were obtained from the appropriate starting materials:

40

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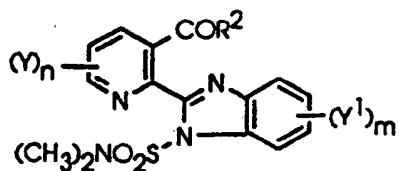
	Cpd	n	Y	m	Y1	m.p./°C
	No					
10	2	1	6-CH ₃	1	4-OCH ₂ CH=CH ₂	141.6-147.5
15	3	1	5-CH ₃	1	4-OCH ₂ CH=CH ₂	101-104
20	4	1	5-C ₂ H ₅	1	4-OCH ₂ CH=CH ₂	137-145
25	5	2	5-CH=CH-CH=CH-6	1	4-OCH ₂ CH=CH ₂	133-135
30	6	0	-	1	4-OCH ₂ C≡CH	174-175
35	Cpd	n	Y	m	Y1	m.p./°C
40	No					
45	7	1	6-CH ₃	1	4-OCH ₂ C≡CH	232-234
50	8	1	5-CH ₃	1	4-OCH ₂ C≡CH	147-149
55	9	2	5-CH=CH-CH=CH-6	1	4-OCH ₂ C≡CH	180 dec.
60	10	1	5-C ₂ H ₅	1	4-OCH ₂ C≡CH	160-161
65	11	0	-	1	4-OCH ₂ C≡CCH ₃	104-107
70	12	2	5-CH=CH-CH=CH-6	1	4-OCH ₂ C≡CCH ₃	176-178
75	13	0	-	1	5-OCH ₂ C≡CH	134.5-134.7

EXAMPLE 2

Preparation of methyl 2-[1-N,N-dimethylsulphamoyl-4-(2-propenoxy)-benzimidazol-2-yl]pyridine-3-carboxylate, compound 16.

A mixture of anhydrous potassium carbonate (11.2g) and methyl 2-[4-(2-propenoxy)-1H-benzimidazol-2-yl]pyridine-3-carboxylat (10g) in acetonitril was stirred at reflux temperature for 2 hours. Then dimethylsulphamoyl chloride (11.63g) was added and the mixture heated at reflux for 12 hours. After cooling and filtration the solvent was evaporated and the resulting oil triturated with ether. The solid thus obtained was purified by chromatography to give the title compound as a white solid, 3.2g, m.p. 127-128°C (Yield: 23%).

By proceeding in a similar manner the following compounds were obtained from the appropriate starting materials:



	Cpd	n	Y	m	Y ¹	R ²	m.p./ °C
	No					**	
15	-	1	6-CH ₃	1	4-OCH ₂ CH=CH ₂	M	not isolated
	14	1	5-CH ₃	1	4-OCH ₂ CH=CH ₂	P	107-111
	-	1	5-C ₂ H ₅	1	4-OCH ₂ CH=CH ₂	M	gum nmr (a)
20	-	2	5-CH=CH-CH=CH-6	1	4-OCH ₂ CH=CH ₂	M	gum nmr (b)
	-	0	-	1	4-OCH ₂ C≡CH	M	170.5-171.5
25	-	1	6-CH ₃	1	4-OCH ₂ C≡CH	M	not isolated
	-	1	5-CH ₃	1	4-OCH ₂ C≡CH	P	107-111
30	-	2	5-CH=CH-CH=CH-6	1	4-OCH ₂ C≡CH	M	175-176
	-	1	5-C ₂ H ₅	1	4-OCH ₂ C≡CH	P	gum nmr (c)
35	-	0	-	1	4-OCH ₂ C≡CCH ₃	M	166-167
	-	2	5-CH=CH-CH=CH-6	1	4-OCH ₂ C≡CCH ₃	M	175-176
40	-	0	-	1	5-OCH ₂ C≡CH	M	nmr (d)

Note:

45

** in the table for R² : M represents -OCH₃; P represents -OCH₂C≡CH.

⁵⁰ H¹NMR.

(a) (DMSO-d₆) d= 1.25 (3H, t), 2.70 (6H s), 3.65 (3H, s), 4.75 (2H,d), 5.3 (1H, d), 5.4 (1H, dd), 6.10 (1H, m), 7.0 (1H, d), 7.4 (1H, t), 7.5 (1H, d), 8.3 (1H, s), 8.8 (1H s) ppm.

(b) (DMSO-d₆) d= 2.85 (6H, s), 3.75 (3H, s), 4.80 (2H, d), 5.30 (1H, d), 5.45 (1H,d), 6.1 (1H, m), 7.00 (1H, d), 7.4 (1H, t), 7.5 (1H, d), 7.85 (1H, t), 8.00 (1H, t), 8.10 (1H, d), 8.35 (1H, d), 9.20 (1H, s) ppm.

(c) (CDCl₃) d= 1.37 (3H, t), 2.20 (1H, t), 2.50 (1H, t), 2.83 (2H, q), 2.88, (6H, s), 4.55 (2H, d), 4.98 (2H, d), 7.00 (1H, d), 7.33 (1H, t), 7.57 (1H, t), 8.30 (1H, d), 8.68 (1H, d) ppm.

(d) (DMSO-d₆) d= 2.85 (6H, s), 3.60 (1H, t), 3.68 (3H, s), 4.41 (2H, d), 7.15 (1H, dd), 7.48 (1H, d), 7.77 (2H, m), 8.45 (1H, d), 8.90 (1H, d) ppm.

EXAMPLE 3.

Preparation of isopropylammonium 2-[1(N,N-dimethylsulphamoyl-4-(2-propenoxy)benzimidazol-2-yl]pyridine-3-carboxylate, compound 15.

5

Isopropylamine (0.1 ml) was added to a stirred solution of 2-[1-(N,N-dimethylsulphamoyl-4-(2-propenoxy)-benzimidazol-2-yl]pyridine-3-carboxylic acid (0.4g) in acetone (10ml). The solution was stirred for 10 minutes and then evaporated to give a white foam which was triturated with hexane to give the title compound (0.36g) as a white hygroscopic solid, m.p. 95-100 °C dec., (Yield: 78%).

10

REFERENCE EXAMPLE 1

Preparation of 7-(2-propenoxy)pyridol[2',3':3,4]pyrrolo[1,2-al]benzimidazol-5-one.

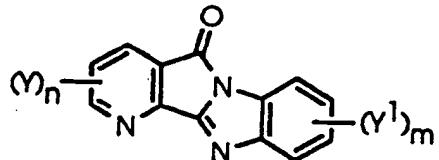
15

A solution of quinolinic anhydride (127g) and 3-(2-propenoxy)-1,2-benzenediamine (140g) in glacial acetic acid was heated at reflux for 3 hours under an inert atmosphere. The mixture was then cooled, acetic anhydride was added and the reaction mixture was heated at reflux for a further 3 hours. After standing for 48 hours at room temperature the resulting crystalline precipitate was filtered and dried to give the title compound as a buff solid, m.p. 173-174.5°C (Yield: 23%).

20

By proceeding in a similar manner the following compounds were obtained from the appropriate starting materials :

25



30

	n	Y	m	Y ¹	m.p./ °C
35	1	2-CH ₃	1	7-OCH ₂ CH=CH ₂	nmr (l)
	1	3-CH ₃	1	7-OCH ₂ CH=CH ₂	194-196
	1	3-C ₂ H ₅	1	7-OCH ₂ CH=CH ₂	171.5-173.5
40	0	-	1	7-OCH ₂ C≡CH	170
	1	2-CH ₃	1	7-OCH ₂ C≡CH	203-205
45	1	3-CH ₃	1	7-OCH ₂ C≡CH	not isolated
	1	3-C ₂ H ₅	1	7-OCH ₂ C≡CH	not isolated
50	0	-	1	7-OCH ₂ C≡CCH ₃	240-242
	0	-	1	8(9)-OCH ₂ C≡CH	not isolated

55

H¹NMR.

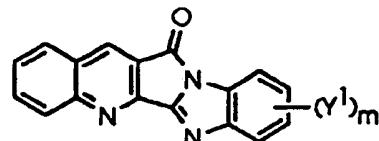
(1) (CDCl₃) δ= 2.6 (3H, s), 4.85 (2H, d), 5.3 (1H, d), 5.5 (1H, d), 6.0-6.2 (1H, m), 6.9 (1H, m), 7.3 (2H, m),

7.4 (1H d), 8.1 (1H, d) ppm.

By proceeding in a similar manner the following compounds were obtained from quinoline-2,3-dicarboxylic acid anhydride and the appropriate 1,2-benzimidazoles :

5

10



15

m	Y1	m.p. / °C
1	4-OCH ₂ CH=CH ₂	nmr (m)
1	4-OCH ₂ C=CH	247-248
1	4-OCH ₂ C=CCH ₃	269-270

20

H¹NMR.

(m) (DMSO-d₆) δ= 4.85 (2H, d), 5.35 (1H, d), 5.50 (1H, d), 6.10 (1H, m), 6.95 (1H, d), 7.40 (2H, m), 7.75 (1H, t), 7.95 (1H, t), 8.15 (2H, t), 8.95 (1H, s) ppm.

25

REFERENCE EXAMPLE 2

25

Preparation of methyl 2-[4-(2-propenylxy)-1H-benzimidazol-2-yl]pyridine-3-carboxylate.

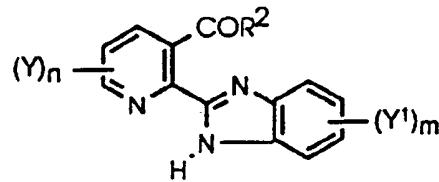
30

A mixture of 7-(2-propenylxy)pyrido[2',3':3,4]pyrrolo[1,2-a]benzimidazol-5-one (54g), triethylamine (22g), and methanol in dichloromethane was stirred at room temperature for 12 hours. The solution was washed successively with water, 0.5M hydrochloric acid, 0.5M sodium hydroxide solution and brine. After drying the solvent was evaporated to give the title compound as a white solid 34.4g, m.p. 122.5-124°C (Yield : 57%).

By proceeding in a similar manner the following compounds were obtained from the appropriate starting materials:

35

40



45

50

55

	n	Y	m	Y¹	R^{2**}	m.p./°C
	1	6-CH ₃	1	4-OCH ₂ CH=CH ₂	M	nmr (e)
5	1	5-CH ₃	1	4-OCH ₂ CH=CH ₂	P	90-92
	1	5-C ₂ H ₅	1	4-OCH ₂ CH=CH ₂	M	gum, nmr (f)
10	2	5-CH=CH-CH=CH-6	1	4-OCH ₂ CH=CH ₂	M	nmr (g)
	0	-	1	4-OCH ₂ C≡CH	M	74-76
15	1	6-CH ₃	1	4-OCH ₂ C≡CH	M	70-72
	1	5-CH ₃	1	4-OCH ₂ C≡CH	P	136.8-141.2
20	2	5-CH=CH-CH=CH-6	1	4-OCH ₂ C≡CH	M	nmr (h)
	1	5-C ₂ H ₅	1	4-OCH ₂ C≡CH	P	gum, nmr (i)
25	0	-	1	4-OCH ₂ C≡CCH ₃	M	gum, nmr (j)
	2	5-CH=CH-CH=CH-6	1	4-OCH ₂ C≡CCH ₃	M	glass, nmr (k)
30	0	-	1	5-OCH ₂ C≡CH	M	not isolated

Note:**

35 In the Table for R² : M represents -OCH₃, P represents -OCH₂C≡CH .

H¹ NMR.

(e) (CDCl₃) δ= 2.6 (3H, s), 4.0 (3H, s), 4.3 (2H, m), 5.2-5.5 (2H, m), 6.1 (1H, br m), 6.7 (1H, d), 7.1-7.3 (3H, m), 7.4 (1H, br s), 7.8 (1H, d) ppm.
 (f) (CDCl₃) δ= 1.25 (3H, t), 2.65 (2H, q), 3.95 (3H, s), 4.70 (2H, d), 5.30 (1H, d), 5.40 (1H, d), 6.00 (1H, m), 6.65 (1H, d), 7.05 (1H, t), 7.20 (1H, d), 7.60 (1H, d), 8.45 (1H, d) ppm.
 (g) (CDCl₃) δ= 4.00 (3H, s), 4.75 (2H, d), 5.25 (1H, d), 5.40 (1H, d), 6.10 (1H, m), 6.05 (1H, d), 7.10 (1H, t), 7.2 (1H, m), 7.55 (1H,t), 7.70 (1H, t), 7.80 (1H, d), 8.05 (1H, d), 8.30 (1H, s) ppm.
 (h) (CDCl₃) δ= 2.55 (1H, t), 4.05 (3H, s), 5.00 (2H, br s), 6.85 (1H, d), 7.20 (1H, t), 7.30 (1H, br d), 7.60 (1H, t), 7.80 (1H, t), 7.85 (1H, d), 8.10 (1H, d), 8.35 (1H, s) ppm.
 (i) (CDCl₃) δ= 1.25 (3H, t), 2.40 (1H, t), 2.45 (1H, t), 2.70 (2H, q), 4.90 (2H, d), 5.05 (2H, d), 6.75 (1H, d), 7.10 (1H, t), 7.20 (1H, d), 7.65 (1H, d), 8.45 (1H, d) ppm.
 (j) (CDCl₃) δ= 1.90 (3H, s), 4.00 (3H, s), 4.80 (2H, s), 6.52 (1H, d), 7.20 (1H, d), 7.25-7.45 (2H, m), 7.87 (1H, d), 8.70 (1H,m), 10.05 ppm.
 (k) (CDCl₃) δ= 1.85 (3H, s), 3.90 (3H, s), 5.05 (2H, s), 6.80 (1H, d), 7.20 (2H, m), 7.77 (1H, t), 7.98 (1H, t), 8.17 (2H, t), 8.70 (1H, s), 13.20 (1H, br s) ppm.

REFERENCE EXAMPLE 3

55

Preparation of 3-(2-propenyoxy)-1,2-bisbenzene diamine.

A mixture of 2-nitro-6-(2-propenyoxy)benzenamine (19.4g) and sodium sulphide (50g) in ethanol and wa-

ter was heated at reflux for 12 hours. The resulting brown solution was then concentrated and reduced pressure and extracted with ethyl acetate. The combined extracts were washed with brine, dried and evaporated to give the title compound as a brown liquid, 12.9g, with the H^1 NMR of the liquid (CDCl_3) giving peaks at $\delta = 3.5$ (4H, b s), 4.6 (2H, d), 5.3-5.5 (2H, dd) 6.0-6.2 (1H, m), 6.4 (2H, m) and 6.7 (1H, t) ppm.

5 By proceeding in a similar manner the following compounds were prepared:

3-(2-propynyoxy)-1,2-benzenediamine, H^1 NMR (DMSO-D_6) 3.52 (1H, t), 4.3 (4H, br s), 4.69 (2H, d), 6.26 (1H, d), 6.30 (1H, d) and 6.48 ppm;

4-(2-propynyoxy)-1,2-benzenediamine as a brown oil.

10 REFERENCE EXAMPLE 4

Preparation of 2-nitro-6-(2-propynyoxy)benzenamine.

Anhydrous potassium carbonate (4.14g) was added portionwise to a stirred solution of 2-amino-3-nitrophenol# (4.62g) in acetone. Allyl bromide (3.63g) was added and the mixture heated at reflux overnight under an inert atmosphere. After cooling the reaction mixture was poured into water and extracted with ethyl acetate. The organic layer was washed successively with 2N sodium carbonate solution, 2N sodium hydroxide solution and brine.

The organic extracts were dried over magnesium sulphate and then evaporated to give the title compound as a dark liquid, 5g, with the H^1 NMR (CDCl_3) giving peaks at $\delta = 4.6$ (2H, d), 5.3 (2H, m), 6.0-6.2 (1H, m), 6.4 (2H, b s), 6.6 (1H, t), 6.9 (1H, d), 7.8 (1H, d) ppm.

20 By proceeding in a similar manner the following compounds were prepared:

2-nitro-6-(2-propynyoxy)benzenamine, m.p. 72-73°C;

2-nitro-4-(2-propynyoxy)benzenamine, m.p. 105.5-106.5°C.

25

REFERENCE EXAMPLE 5.

Preparation of 3-(2-butynyoxy)-1,2-benzenediamine.

A solution of concentrated hydrochloric acid (3 ml) in 50% aqueous ethanol (9 ml) was added to a stirred suspension of iron powder (23.5 g) and 4-(2-butynyoxy)-2,1,3-benzoxadiazole (13.2 g) in 50% aqueous ethanol (70 ml) and heated at reflux for 24 hours. The reaction mixture was then basified whilst still hot, to pH 10, by the addition of a 15% solution of potassium hydroxide in ethanol. The reaction mixture was then filtered hot, and the filtrate evaporated to dryness. The black residue was dissolved in water, filtered and the filtrate extracted with dichloromethane. Drying and evaporation of the organic phase gave the title compound (10.35 g) as a dark brown oil, (Yield : 84%), H^1 NMR (DMSO-D_6) 1.83 (3H, s), 4.00 (2H, br s), 4.50 (2H, br s), 4.64 (2H, s), 6.28 (2H, m), 6.38 (1H, t) ppm.

35 By proceeding in a similar manner 3-(but-3-yn-1-oxy)-1,2-benzene-diamine, was prepared, H^1 NMR (DMSO-D_6) 2.38 (1H, br s), 2.55 (2H, m), 3.8 (4H, m), 4.3 (2H, br s), 6.2 (2H, m), 6.3 (1H, m) ppm.

40

REFERENCE EXAMPLE 6

Preparation of 4-(2-butynyoxy)-2,1,3-benzoxadiazole.

45 4-Fluoro-2,1,3-benzoxadiazole (0.5 g) was added to a stirred suspension of anhydrous potassium carbonate (0.75 g) in 2-butyn-1-ol (0.38 g), and acetone (5 ml). The reaction mixture was stirred at ambient temperature for 3 hours then heated at reflux for 20 hours. The reaction mixture was allowed to cool, poured on to water and extracted with ether. The ethereal extracts were combined, washed with water, dried and evaporated to give the title compound (0.44 g) as a pale yellow solid, (Yield : 65%), H^1 NMR (DMSO-D_6) $\delta = 1.88$ (3H, t), 5.05 (2H, q), 6.92 (1H, m), 7.57 (2H, m) ppm.

50 By proceeding in a similar manner 4-(but-3-yn-1-oxy)-2,1,3-benzoxadiazole was prepared, H^1 NMR (DMSO-D_6) 2.49 (1H, t), 2.78 (2H, m), 4.35 (2H, t), 6.90 (1H, d), 7.5 (2H, m) ppm.

55 According to a feature of the present invention, there is provided a method for controlling the growth of weeds (i.e. undesired vegetation) at a locus which comprises applying to the locus a herbicidally effective amount of at least one benzimidazolyl derivative of general formula (I) or an agriculturally acceptable salt thereof. For this purpose, the benzimidazolyl derivatives are normally used in the form of herbicides compositions

#As described by E. Fourneau and J. Tréfouillet, Bull. Soc. Chim. Franc., 1927, 41, 448.

(i. . in association with compatible diluents or carriers and/or surface active agents suitable for use in herbicidal compositions), for example as hereinbefore described.

The compounds of general formula (I) show herbicidal activity against dicotyledonous (i.e. broad-leaved) and monocotyledonous (e.g. grass) weeds by pre- and/or post-emergence application.

By the term "pre-emergence application" is meant application to the soil in which the weed seeds or seedlings are present before emergence of the weeds above the surface of the soil. By the term "post-emergence application" is meant application to the aerial or exposed portions of the weeds which have emerged above the surface of the soil. For example, the compounds of general formula (I) may be used to control the growth of:

broad-leaved weeds, for example, *Abutilon theophrasti*, *Amaranthus retroflexus*, *Bidens pilosa*, *Chenopodium album*, *Galium aparine*, *Ipomoea* spp. e.g. *Ipomoea purpurea*, *Sesbania exaltata*, *Sinapis arvensis*, *Solanum nigrum* and *Xanthium strumarium*, and

grass weeds, for example *Alopecurus myosuroides*, *Avena fatua*, *Digitaria sanguinalis*, *Echinochloa crus-galli*, *Eleusine indica* and *Setaria* spp. e.g. *Setaria faberii* or *Setaria viridis*, and

sedges, for example, *Cyperus esculentus*.

The amounts of compounds of general formula (I) applied vary with the nature of the weeds, the compositions used, the time of application, the climatic and edaphic conditions and (when used to control the growth of weeds in crop-growing areas) the nature of the crops. When applied to a crop-growing area, the rate of application should be sufficient to control the growth of weeds without causing substantial permanent damage to the crop. In general, taking these factors into account, application rates between 0.01kg and 5kg of active material per hectare give good results. However, it is to be understood that higher or lower application rates may be used, depending upon the particular problem of weed control encountered.

The compounds of general formula (I) may be used to control selectively the growth of weeds, for example to control the growth of those species hereinbefore mentioned, by pre- or post-emergence application in a directional or non-directional fashion, e.g. by directional or non-directional spraying, to a locus of weed infestation which is an area used, or to be used, for growing crops, for example cereals, e.g. wheat, barley, oats, maize and rice, soya beans, field and dwarf beans, peas, lucerne, cotton, peanuts, flax, onions, carrots, cabbage, oilseed rape, sunflower, sugar beet, and permanent or sown grassland before or after sowing of the crop or before or after emergence of the crop. For the selective control of weeds at a locus of weed infestation which is an area used or to be used, for growing of crops, e.g. the crops hereinbefore mentioned, application rates between 0.01kg and 4.0kg, and preferably between 0.01kg and 2.0kg, of active material per hectare are particularly suitable.

The compounds of general formula (I) may also be used to control the growth of weeds, especially those indicated above, by pre- or post-emergence application in established orchards and other tree-growing areas, for example forests, woods and parks, and plantations, e.g. sugar cane, oil palm and rubber plantations. For this purpose they may be applied in a directional or non-directional fashion (e.g. by directional or non-directional spraying) to the weeds or to the soil in which they are expected to appear, before or after planting of the trees or plantations at application rates between 0.25kg and 5.0kg, and preferably between 0.5kg and 4.0kg of active material per hectare.

The compounds of general formula (I) may also be used to control the growth of weeds, especially those indicated above, at loci which are not crop-growing areas but in which the control of weeds is nevertheless desirable.

Examples of such non-crop-growing areas include airfields, industrial sites, railways, roadside verges, the verges of rivers, irrigation and other waterways, scrublands and fallow or uncultivated land, in particular where it is desired to control the growth of weeds in order to reduce fire risks. When used for such purposes in which a total herbicidal effect is frequently desired, the active compounds are normally applied at dosage rates higher than those used in crop-growing areas as hereinbefore described. The precise dosage will depend upon the nature of the vegetation treated and the effect sought.

Pre- or post-emergence application, and preferably pre-emergence application, in a directional or non-directional fashion (e.g. by directional or non-directional spraying) at application rates between 1.0kg and 20.0kg, and preferably between 5.0 and 10.0kg, of active material per hectare are particularly suitable for this purpose.

When used to control the growth of weeds by pre-emergence application, the compounds of general formula (I) may be incorporated into the soil in which the weeds are expected to emerge. It will be appreciated that when the compounds of general formula (I) are used to control the growth of weeds by post-emergence application, i.e. by application to the aerial or exposed portions of emerging weeds, the compounds of general formula (I) will also normally come into contact with the soil and may also then exercise a pre-emergence control on later-germinating weeds in the soil.

Where especially prolonged weed control is required, the application of the compounds of general formula

(I) may be repeated if required.

According to a further feature of the present invention, there are provided compositions suitable for herbicides comprising one or more of the benzimidazolyl derivatives of general formula I or an agriculturally acceptable salt thereof, in association with, and preferably homogeneously dispersed in, one or more compatible agriculturally-acceptable diluents or carriers and/or surface active agents [i.e. diluents or carriers and/or surface active agents of the type generally accepted in the art as being suitable for use in herbicidal compositions and which are compatible with compounds of general formula (I)]. The term "homogeneously dispersed" is used to include compositions in which the compounds of general formula (I) are dissolved in other components. The term "herbicidal compositions" is used in a broad sense to include not only compositions which are ready for use as herbicides but also concentrates which must be diluted before use. Preferably, the compositions contain from 0.05 to 90% by weight of one or more compounds of general formula (I).

The herbicidal compositions may contain both a diluent or carrier and surface-active (e.g. wetting, dispersing, or emulsifying) agent. Surface-active agents which may be present in herbicidal compositions of the present invention may be of the ionic or non-ionic types, for example sulphoricinoleates, quaternary ammonium derivatives, products based on condensates of ethylene oxide with alkyl and polyaryl phenols, e.g. nonyl- or octyl-phenols, or carboxylic acid esters of anhydrosorbitols which have been rendered soluble by etherification of the free hydroxy groups by condensation with ethylene oxide, alkali and alkaline earth metal salts of sulphuric acid esters and sulphonics acids such as dinonyl- and dioctyl-sodium sulphonosuccinates and alkali and alkaline earth metal salts of high molecular weight sulphonics acid derivatives such as sodium and calcium lignosulphonates and sodium and calcium alkylbenzene sulphonates.

Suitably, the herbicidal compositions according to the present invention may comprise up to 10% by weight, e.g. from 0.05% to 10% by weight, of surface-active agent but, if desired, herbicidal compositions according to the present invention may comprise higher proportions of surface-active agent, for example up to 15% by weight in liquid emulsifiable suspension concentrates and up to 25% by weight in liquid water soluble concentrates.

Examples of suitable solid diluents or carriers are aluminium silicate, talc, calcined magnesia, kieselguhr, tricalcium phosphate, powdered cork, adsorbent carbon black and clays such as kaolin and bentonite. The solid compositions (which may take the form of dusts, granules or wettable powders) are preferably prepared by grinding the compounds of general formula (I) with solid diluents or by impregnating the solid diluents or carriers with solutions of the compounds of general formula (I) in volatile solvents, evaporating the solvents and, if necessary, grinding the products so as to obtain powders. Granular formulations may be prepared by absorbing the compounds of general formula (I) (dissolved in suitable solvents, which may, if desired, be volatile) onto the solid diluents or carriers in granular form and, if desired, evaporating the solvents, or by granulating compositions in powder form obtained as described above. Solid herbicides compositions, particularly wettable powders and granules, may contain wetting or dispersing agents (for example of the types described above), which may also, when solid, serve as diluents or carriers.

Liquid compositions according to the invention may take the form of aqueous, organic or aqueous-organic solutions, suspensions and emulsions which may incorporate a surface-active agent. Suitable liquid diluents for incorporation in the liquid compositions include water, glycols, tetrahydrofurfuryl alcohol, acetophenone, cyclohexanone, isophorone, toluene, xylene, mineral, animal and vegetable oils and light aromatic and naphthenic fractions of petroleum (and mixtures of these diluents). Surface-active agents, which may be present in the liquid compositions, may be ionic or non-ionic (for example of the types described above) and may, when liquid, also serve as diluents or carriers.

Powders, dispersible granules and liquid compositions in the form of concentrates may be diluted with water or other suitable diluents, for example mineral or vegetable oils, particularly in the case of liquid concentrates in which the diluent or carrier is an oil, to give compositions ready for use.

When desired, liquid compositions of the compound of general formula (I) may be used in the form of self-emulsifying concentrates containing the active substances dissolved in the emulsifying agents or in solvents containing emulsifying agents compatible with the active substances, the simple addition of water to such concentrates producing compositions ready for use.

Liquid concentrates in which the diluent or carrier is an oil may be used without further dilution using the electrostatic spray technique.

Herbicidal compositions according to the present invention may also contain, if desired, conventional adjuvants such as adhesives, protective colloids, thickeners, penetrating agents, stabilisers, sequencing agents, anti-caking agents, colouring agents and corrosion inhibitors. These adjuvants may also serve as carriers or diluents.

Unless otherwise specified, the following percentages are by weight. Prepared herbicides compositions according to the present invention are aqueous suspension concentrates which comprise from 10 to 70% of

n or more compounds of general formula (I), from 2 to 10% of surface-active agent, from 0.1 to 5% of thickener and from 15 to 87.9% of water;

water soluble powders which comprise from 10 to 90% of n or more compounds of general formula (I), from 2 to 10% of surface-active agent and from 8 to 88% of solid diluents or carriers;

5 water soluble or water dispersible powders which comprise from 10 to 90% of one or more compounds of general formula (I), from 2 to 40% of sodium carbonate and from 0 to 88% of solid diluent;

liquid water soluble concentrates which comprise from 5 to 50%, e.g. 10 to 30%, of one or more compounds of general formula (I), from 5 to 25% of surface-active agent and from 25 to 90%, e.g. 45 to 85%, of water miscible solvent, e.g. dimethylformamide, or a mixture of water-miscible solvent and water;

10 liquid emulsifiable suspension concentrates which comprise from 10 to 70% of one or more compounds of general formula (I), from 5 to 15% of surface-active agent, from 0.1 to 5% of thickener and from 10 to 84.9% of organic solvent;

granules which comprise from 1 to 90%, e.g. 2 to 10% of one or more compounds of general formula (I), from 0.5 to 7%, e.g. 0.5 to 2%, of surface-active agent and from 3 to 98.5%, e.g. 88 to 97.5%, of granular carrier and

15 emulsifiable concentrates which comprise 0.05 to 90%, and preferably from 1 to 60% of one or more compounds of general formula (I), from 0.01 to 10%, and preferably from 1 to 10%, of surface-active agent and from 9.99 to 99.94%, and preferably from 39 to 98.99%, of organic solvent.

Herbicidal compositions according to the present invention may also comprise the compounds of general

20 formula (I) in association with, and preferably homogeneously dispersed in, one or more other pesticidally active compounds and, if desired, one or more compatible pesticidally acceptable diluents or carriers, surface-active agents and conventional adjuvants as hereinbefore described. Examples of other pesticidally active compounds which may be included in, or used in conjunction with, the herbicidal compositions of the present invention include herbicides, for example to increase the range of weed species controlled for example alachlor

25 [2-chloro-2',6'-diethyl-N-(methoxy-methyl)-acetanilide], atrazine [2-chloro-4-ethylamino-6-isopropyl-amino-1,3,5-triazine], bromoxynil [3,5-dibromo-4-hydroxybenzonitrile], chlortoluron [N'-(3-chloro-4-methylphenyl)-N,N-dimethylurea], cyanazine [2-chloro-4-(1-cyano-1-methylethylamino)-6-ethylamino-1,3,5-triazine], 2,4-D [2,4dichlorophenoxy-acetic acid], dicamba [3,6-dichloro-2-methoxybenzoic acid], difenzoquat [1,2-dimethyl-3,5-diphenyl-pyrazolium salts], flampropmethyl [methyl N-2-(N-benzoyl-3-chloro-4-fluoroanilino)-propionate], fluometuron [N'-(3-trifluoro-methylphenyl)-N,N-dimethylurea], isoproturon [N'-(4-isopropyl-phenyl)-N,N-dimethylurea], nicosulfuron [2-(4',6'dimethoxypyrimidin-2'-ylcarbamoylsulfamoyl)-N,N-dimethylnicotinamide], insecticides, e.g. synthetic pyrethroids, e.g. permethrin and cypermethrin, and fungicides, e.g. carbamates, e.g. methyl N-(1-butyl-carbamoyl-benzimidazol-2-yl)carbamate, and aiazoles e.g. 1-(4-chloro-phenoxy)-3,3-dimethyl-1-(1,2,4-triazol-1-yl)-butan-2-one.

35 Pesticidally active compounds and other biologically active materials which may be included in, or used in conjunction with, the herbicidal compositions of the present invention, for example those hereinbefore mentioned, and which are acids, may, if desired be utilized in the form of conventional derivatives, for example alkali metal and amine salts and esters.

According to a further feature of the present invention there is provided an article of manufacture comprising 40 at least one of the benzimidazolyl derivatives of general formula (I) or, as is preferred, a herbicidal composition as hereinbefore described, and preferably a herbicides concentrate which must be diluted before use, comprising at least one of the benzimidazolyl derivatives of general formula (I) within a container for the aforesaid derivative or derivatives of general formula (I), or a said herbicides composition, and instructions physically associated with the aforesaid container setting out the manner in which the aforesaid derivative or derivatives of general formula (I) or herbicidal composition contained therein is to be used to control the growth of weeds. The containers will normally be of the types conventionally used for the storage of chemical substances which are solid at normal ambient temperatures and herbicidal compositions particularly in the form of concentrates, for example cans and drums of metal, which may be internally lacquered, and plastics materials, bottles or glass and plastics materials and, when the contents of the container is a solid, for example granular, herbicidal compositions, boxes, for example of cardboard, plastics materials and metal, or sacks. The containers will normally be of sufficient capacity to contain amounts of the benzimidazolyl derivative or herbicides compositions sufficient to treat at least one acre of ground to control the growth of weeds therein but will not exceed a size which is convenient for conventional methods of handling. The instructions will be physically associated with the container, for example by being printed directly thereon or on a label or tag affixed thereto. The directions will normally indicate that the contents of the container, after dilution if necessary, are to be applied to control the growth of weeds at rates of application between 0.01kg and 20kg of active material per hectare in the manner and for the purposes hereinabove described.

The following Examples illustrate herbicidal compositions according to the present invention:

EXAMPLE C1

A soluble concentrat was formed from :

5	Active ingredient (compound 1)	20% w/v
	Potassium hydroxide solution 33% w/v	10% v/v
10	Tetrahydrofurfuryl alcohol (THFA)	10% v/v
	Water	to 100 volumes.

by stirring THFA, active ingredient (compound 1) and 90% volume of water and slowly adding the potassium hydroxide solution until a steady pH7-8 was obtained then making up to volume with water.

Similar soluble concentrates may be prepared as described above by replacing the benzimidazolyl derivative (compound 1) with other compounds of general formula (I).

EXAMPLE C2

20 A wettable powder was formed from :

25	Active ingredient (compound 1)	50% w/w
	Sodium dodecylbenzene sulphonate	3% w/w
	Sodium lignosulphate	5% w/w
30	Sodium formaldehyde alkylnaphthalene sulphonate	2% w/w
	Microfine silicon dioxide	3% w/w and
	China clay	37% w/w

35 by blending the above ingredients together and grinding the mixture in an air jet mill.

Similar wettable powders may be prepared as described above by replacing the benzimidazolyl derivative (compound 1) with other compounds of general formula (I).

EXAMPLE C3

A water soluble powder was formed from :

45	Active ingredient (compound 1)	50% w/w
	Sodium dodecylbenzenesulphonate	1% w/w
	Microfine silicon dioxide	2% w/w
50	Sodium bicarbonate	47% w/w

by mixing the above ingredients and grinding th above mixtur in a hamm r mill.

Similar wat r solubl powd rs may b pr pared as d scribed above by replacing th b nzimidazolyl derivativ (compound 1) with oth r compounds of g n al formula (I).

Repres ntative compounds of general formula (I) have been used in h rbicidal applications according to the following procedures.

METHOD OF USE OF HERBICIDAL COMPOUNDS:

a) General

5 Appropriate quantities of the compounds used to treat the plants were dissolved in acetone to give solutions equivalent to application rates of up to 4000g test compound per hectare (g/ha). These solutions were applied from a standard laboratory herbicide sprayer delivering the equivalent of 290 litres of spray fluid hectare.

b) Weed control : Pre-emergence

10 The seeds were sown in 70 mm square, 75 mm deep plastic pots in non-sterile soil. The quantities of seed per pot were as follows:-

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	<u>Weed species</u>	<u>Approx number of seeds/pot</u>
1) Broad-leaved weeds		
5	Abutilon theophrasti	10
	Amaranthus retroflexus	20
10	Galium aparine	10
	Ipomoea purpurea	10
	Sinapis arvensis	15
15	Xanthium strumarium	2.
2) Grass weeds		
20	Alopecurus myosuroides	15
	Avena fatua	10
	Echinochloa crus-galli	15
25	Setaria viridis	20.
3) Sedges		
30	Cyperus esculentus	3.

	<u>Crop</u>	
1) Broad-leaved		
35	Cotton	3
	Soya	3.
2) Grass		
40	Maize	2
45	Rice	6
	Wheat	6.

50 The compounds of the invention were applied to the soil surface, containing the seeds, as described in (a). A single pot of each crop and each weed was allocated to each treatment, with unsprayed controls and controls sprayed with acetone alone.

55 After treatment the pots were placed on capillary matting kept in a glass house, and watered overhead. Visual assessment of crop damage was made 20-24 days after spraying. The results were expressed as the percentage reduction in growth or damage to the crop or weeds, in comparison with the plants in the control pots.

c) Weed control : Post- emergence

5 The weeds and crops were sown directly into John Innes potting compost in 75 mm depth, 70 mm square pots except for Amaranthus which was pricked out at the seedling stage and transferred to the pots one week before spraying. The plants were then grown in the greenhouse until ready for spraying with the compounds used to treat the plants. The number of plants per pot were as follows :-

1) Broad leafed weeds

10	<u>Weed species</u>	<u>Number of plants per pot</u>	<u>Growth stage</u>
15	Abutilon theophrasti	3	1-2 leaves
	Amaranthus retroflexus	4	1-2 leaves
	Galium aparine	3	1st whorl
20	Ipomoea purpurea	3	1-2 leaves
	Sinapis arvensis	4	2 leaves
	Xanthium strumarium	1	2-3 leaves.

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2) Grass weeds

	<u>Weed species</u>	<u>Number of plants per pot</u>	<u>Growth stage</u>
5	Alopecurus myosuroides	8-12	1-2 leaves
	Avena fatua	12-18	1-2 leaves
10	Echinochloa crus-galli	4	2-3 leaves
	Setaria viridis	15-25	1-2 leaves.

15 3) Sedges

	<u>Weed species</u>	<u>Number of plants per pot</u>	<u>Growth stage</u>
20	Cyperus esculentus	3	3 leaves.

1) Broad leafed

	<u>Crops</u>	<u>Number of plants per pot</u>	<u>Growth stage</u>
25	Cotton	2	1 leaf
	Soya	2	2 leaves.

30

2) Grass

	<u>Crops</u>	<u>Number of plants per pot</u>	<u>Growth stage</u>
35	Maize	2	2-3 leaves
	Rice	4	2-3 leaves
40	Wheat	5	2-3 leaves.

45 The compounds used to treat the plants were applied to the plants as described in (a). A single pot of each crop and weed species was allocated to each treatment, with unsprayed controls and controls sprayed with acetone alone.

After treatment the pots were placed on capillary matting in a glass house, and watered overhead once after 24 hours and then by controlled sub-irrigation. Visual assessment of crop damage and weed control was made 20-24 days after spraying. The results were expressed as the percentage reduction in growth or damage to the crop or weeds, in comparison with the plants in the control pots.

50 Representative compounds of the invention, used at 4000 g/ha or less, have shown an excellent level of herbicidal activity in the foregoing experiments, giving 90% reduction in growth of one or more weed species when applied pre- or post- emergence, combined with tolerance on one or more crops.

When applied pre- emergence, at 1000 g/ha compounds 4, 5, 9, 11, 12, 14 and 15 gave at least 90% reduction in growth of one or more weed species combined with tolerance on one or more crops.

55 When applied post- emergence at 1000 g/ha compounds 2, 3, 5, 7, 8, 9, 12, and 14 gave at least 90% reduction in growth of one or more weed species combined with tolerance on one or more crops.

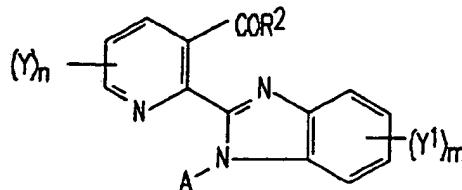
When applied pre- emergence at 1000 g/ha compounds 1, 2, 3, 6, 7, 8 and 15 gave at least 90% reduction in growth of all weed species.

When applied post-emergence at 250 g/ha compounds 1 and 6 gave at least 90% reduction in growth of one or more weed species combined with tolerance on one or more crops.

5 Claims

1. A benzimidazolyl derivative of general formula I:-

10



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wherein

Y represents:

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a straight- or branched- chain alkyl, alkenyl or alkynyl group containing up to eight carbon atoms optionally substituted by one or more groups R¹, which may be the same or different; or
a group selected from -OR, -SR, -SO₂R³, halogen, O-aryl, cyano, -NR⁴R⁵, aryl, aralkyl, nitro, or

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a cycloalkyl group containing from 3 to 6 carbon atoms optionally substituted by one or more R¹ groups which may be the same or different;

Y¹ represents:-

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a straight- or branched- chain alkyl, alkenyl or alkynyl group containing up to eight carbon atoms which is optionally substituted by one or more R¹ groups which may be the same or different; or
a cycloalkyl group containing from 3 to 6 carbon atoms optionally substituted by one or more R¹ groups which may be the same or different; or

a group selected from -SR, -OR, -OR^{1a}, halogen, aryl, aralkyl, O-aryl or -NR⁷R⁸;R² represents:-a group -OH or -NR⁷R⁸;

or -X-M, where X represents oxygen or sulphur, and

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M represents:-

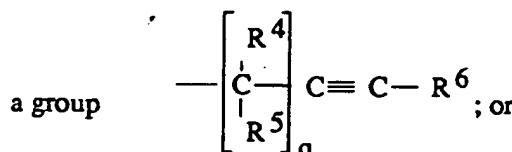
a straight- or branched- chain alkyl group containing up to eight carbon atoms optionally substituted by one or more R¹ groups which may be the same or different; or

a cycloalkyl group containing from 3 to 6 carbon atoms optionally substituted by one or more R¹ groups which may be the same or different; or

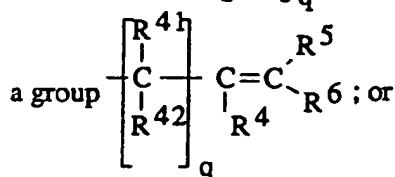
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a group selected from aryl and aralkyl; or

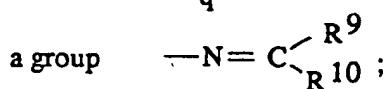
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A represents a group - SO₂B;

B represents:-

a straight- or branch d- chain alkyl group containing up to 6 carbon atoms optionally substituted by one or more groups, which may be the same or different, selected from -OR³, -SR³ and halogen;

5 or

a cycloalkyl group containing from 3 to 8 carbon atoms optionally substituted by one or more groups, which may be the same or different; selected from -OR³, -SR³, R³ and halogen; or

a group selected from aryl, aralkyl and -NR⁷R⁸;

R represents:-

10 a straight- or branched- chain alkyl group containing up to eight carbon atoms optionally substituted by one or more groups R¹ which may be the same or different; or

a cycloalkyl group containing from 3 to 6 carbon atoms optionally substituted by one or more groups R³ which may be the same or different;

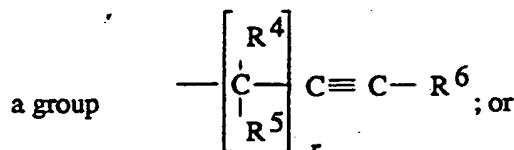
R¹ represents:-

15 a cycloalkyl group containing from 3 to 6 carbon atoms; or

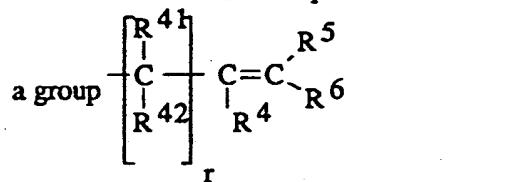
a group selected from -OR³, -SR³, halogen, R³ or O-aryl;

R^{1a} represents:-

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R³ represents a straight- or branched- chain alkyl group containing up to 6 carbon atoms optionally substituted by one or more halogen atoms which may be the same or different;

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R⁴, R⁴¹, R⁴² and R⁵, which may be the same or different, each represent hydrogen or a straight- or branched- chain alkyl group containing up to 6 carbon atoms optionally substituted by one or more halogen atoms which may be the same or different; or aryl;

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R⁶ represents a group selected from R⁴ or aralkyl;

R⁷ and R⁸, which may be the same or different, each represent:-

a hydrogen atom, or

a group selected from R, -OR³, -SR³, halogen, R³ or O-aryl, aryl or aralkyl; or R⁷ and R⁸ may form together with the nitrogen to which they are attached a heterocycle containing from 3 to 6 carbon atoms in the ring and zero, 1 or 2 additional heteroatoms in the ring selected from nitrogen, oxygen and sulphur;

45

R⁹ and R¹⁰, which may be the same or different, each represent:

a hydrogen atom, or

a straight- or branched- chain alkyl group containing up to eight carbon atoms optionally substituted by one or more groups, which may be the same or different, selected from halogen, -OR or -S(O)_sR, where s is zero, 1 or 2; or a phenyl group optionally substituted by from one to four groups, which may be the same or different, selected from nitro, R, -NR⁷R⁸, halogen or -S(O)_sR; or

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a 5 or 6 membered heterocycle containing from 3 to 5 carbon atoms in the ring and one or more heteroatoms in the ring selected from nitrogen, sulphur or oxygen, optionally substituted by one or more groups R¹ which may b th same or different;

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or R⁹ and R¹⁰ may form together with the nitrogen to which they ar attach d a h terocycl containing 4 or 5 carbon atoms in th ring, which may be optionally substitut d by from 1 to 3 groups R³ which may b the same or different;

'aryl' repres nts:-

a phenyl group optionally substitut d by from 1 to 4 groups which may b th same or dif-

f rent s lect d from -OR³, -SR³, halogen or R³; or
 a 5 or 6 m mbered heterocycle containing from 3 to 5 carbon atoms in th ring and one or
 mor h teratoms in th ring sel ct d from nitrogen, sulphur or oxyg n, optionally substituted by on or
 more groups, which may be the sam or diff rent, sel ct d from -OR³, -SR³, halogen or R³;

5 'aralkyl' represents a group -(CR⁴R⁵)_p-aryl;
 m represents an integer from 1 to 4, the groups Y¹ being the same or different when m is greater
 than 1;
 n represents zero, or an integer from 1 to 3;
 p represents one or two;

10 q represents an integer from one to three;
 r represents an integer from one to five;
 when r, p or q is greater than one, the groups -CR⁴ R⁵- and the groups -CR⁴¹R⁴²- may be the same
 or different;
 with the proviso that one of the groups Y¹ represents -OR^{1a}, in either the 4-position or the 5-position
 15 of the benzimidazole ring;
 where n represents 2 or 3, two groups Y which are adjacent to each other in the 5- and 6- positions on the pyridine ring can, with the carbon atoms to which they attached, form a fused phenyl ring, or
 can form an aliphatic or aromatic ring having 5 or 6 atoms in the ring and having not more than 2 heteroatoms in the ring selected from oxygen and sulphur;

20 and agriculturally acceptable salts thereof.

2. A compound according to claim 1 wherein:

- (a) A represents -SO₂NR⁷R⁸; and/or
- (b) R² represents -OH or -XM; and/or
- (c) Y represents an alkyl group containing one or two carbon atoms optionally substituted by one or
 25 more halogen atoms; and/or
- (d) Y¹ represents -OR, halogen, -OR^{1a} or -NR⁷R⁸; and/or
- (e) m represents one or two; and/or
- (f) R⁷ and R⁸, which may be the same or different, each represent a straight- or branched- chain alkyl
 30 group containing up to 4 carbon atoms optionally substituted by one or more atoms which may be the
 same or different selected from fluorine or chlorine; and/or
- (g) X represents oxygen; and/or
- (h) R⁴, R⁴¹, R⁴², R⁵ and R⁶, which may be the same or different, each represent hydrogen or a straight-
 35 or branched- chain alkyl group containing up to 4 carbon atoms optionally substituted by one or more
 halogen atoms;and/or
- (i) n represents zero, one or two; and/or
- (j) r represents one or two.

3. A compound according to claim 1 or 2 wherein:

B represents -SO₂NMe₂;

40 R² represents -OH or -X-M;

X represents oxygen;

M represents a methyl or propynyl group, or a potassium or isopropylammonium cation;

Y¹ represents -OR^{1a} in the 4-position of the benzimidazole ring;

45 R^{1a} represents 2-propenyl, 2-propynyl or 2-butynyl ;

Y represents methyl, ethyl, or two groups Y in the 5- and 6- positions of the pyridine ring together
 with the carbon atoms to which they are attached form a fused phenyl ring;

m represents one; and

n represents one or two.

50 4. A compound according to claim 1, 2 or 3 which is:

2-[1-(N,N-dimethylsulphamoyl)-4-(2-propenoxy)benzimidazol-2-yl]pyridine-3-carboxylic acid;

2-[1-(N,N-dimethylsulphamoyl)-4-(2-propenoxy)benzimidazol-2-yl]-6-methylpyridine-3-car-
 boxylic acid;

55 2-[1-(N,N-dimethylsulphamoyl)-4-(2-propenoxy)benzimidazol-2-yl]-5-methylpyridine-3-car-
 boxylic acid;

2-[1-(N,N-dimethylsulphamoyl)-4-(2-propenoxy)benzimidazol-2-yl]-5-thiopyridine-3-carbox-
 ylic acid;

acid; 2-[1-(N,N-dimethylsulphamoyl)-4-(2-propynoxy)benzimidazol-2-yl]quinoline-3-carboxylic acid;

5 acid; 2-[1-(N,N-dimethylsulphamoyl)-4-(2-propynoxy)benzimidazol-2-yl]pyridine-3-carboxylic acid; 2-[1-(N,N-dimethylsulphamoyl)-4-(2-propynoxy)benzimidazol-2-yl]-6-methylpyridine-3-carboxylic acid;

10 acid; 2-[1-(N,N-dimethylsulphamoyl)-4-(2-propynoxy)benzimidazol-2-yl]-5-methylpyridine-3-carboxylic acid; 2-[1-(N,N-dimethylsulphamoyl)-4-(2-propynoxy)benzimidazol-2-yl]quinoline-3-carboxylic acid;

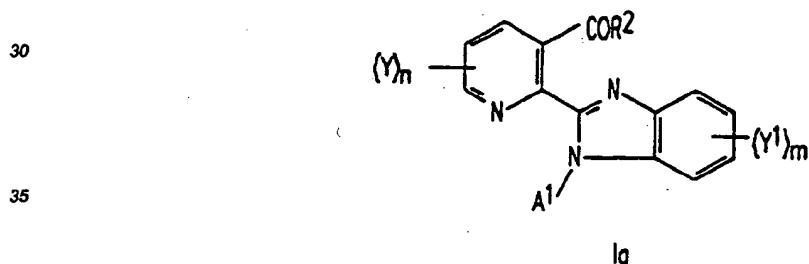
15 acid; 2-[1-(N,N-dimethylsulphamoyl)-4-(2-propynoxy)benzimidazol-2-yl]-5-ethylpyridine-3-carboxylic acid; 2-[1-(N,N-dimethylsulphamoyl)-4-(2-butynoxy)benzimidazol-2-yl]pyridine-3-carboxylic acid; 2-[1-(N,N-dimethylsulphamoyl)-4-(2-butynoxy)benzimidazol-2-yl]quinoline-3-carboxylic acid; 2-[1-(N,N-dimethylsulphamoyl)-5-(2-propynoxy)benzimidazol-2-yl]pyridine-3-carboxylic acid; or an agriculturally acceptable salt thereof, or

20 2-propynyl 2-[1-(N,N-dimethylsulphamoyl)-4-(2-propynoxy)benzimidazol-2-yl]-5-methylpyridine-3-carboxylate; isopropylammonium 2-[1-(N,N-dimethylsulphamoyl)-4-(2-propenyl)benzimidazol-2-yl]pyridine-3-carboxylate; or

25 methyl 2-[1-(N,N-dimethylsulphamoyl)-4-(2-propenyl)benzimidazol-2-yl]pyridine-3-carboxylate.

5. A process for the preparation of a compound of general formula (I) according to claim 1 which comprises:

25 a) where R² is a -XM or -NR⁷R⁸ radical, the reaction of a compound of the formula CISO₂B with a compound of formula (Ia):



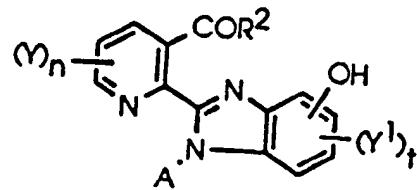
40 in which A¹ is the hydrogen atom, R² is an -XM or -NR⁷R⁸ radical and the other symbols are as defined in claim 1,

45 in the presence of an acid acceptor;

b) where R² represents -OH, by the hydrolysis of a compound of formula (I) in which R² represents the group -XM;

c) where m represents 1 or 2, one of the groups Y1 represents a group -OR^{1a} which occupies the 4- or 5-position of the benzimidazole ring, R² represents a group -X-M wherein X is oxygen and M represents a straight- or branched-chain alkyl group containing up to 8 carbon atoms optionally substituted by one or more R¹ groups which may be the same or different, or a cycloalkyl group containing from 3 to 6 carbon atoms optionally substituted by one or more R¹ groups which may be the same or different and the group Y is as defined in claim 1 excluding an alkenyl or alkynyl group or chlorine, bromine or iodine,

50 the reaction of a hydroxybenzimidazole of formula (XIV):



10 wherein t is 0 or 1 and the hydroxy group occupies the 4- or 5-position of the benzimidazole ring, with a compound R^{1a}-L where L represents a leaving group, to convert the hydroxy group in the 4- or 5-position of the benzimidazole ring into a group -OR^{1a};

15 optionally followed by the conversion of a compound of formula (I) thus obtained into a salt thereof.

20 6. A herbicidal composition which comprises as active ingredient a herbicidally effective amount of a benzimidazolyl derivative of general formula (I) according to any one of claims 1 to 4 or an agriculturally acceptable salt thereof, in association with an agriculturally acceptable diluent or carrier and/or surface active agent.

25 7. A herbicidal composition according to claim 6 which comprises 0.05 to 90% by weight of active ingredient.

8. A herbicidal composition according to claim 6 or 7 which is in liquid form and contains from 0.05 to 25% by weight of surface-active agent.

30 9. A herbicidal composition according to any one of claims 6, 7 or 8 in the form of an aqueous suspension concentrate, a wettable powder, a water soluble or water dispersible powder, a liquid water soluble concentrate, a liquid emulsifiable suspension concentrate, a granule or an emulsifiable concentrate.

35 10. A method for controlling the growth of weeds at a locus which comprises applying to the locus a herbicidally effective amount of a benzimidazolyl derivative of general formula (I) according to any one of claims 1 to 4 or an agriculturally acceptable salt thereof.

11. A method according to claim 10 in which the locus is an area used, or to be used for growing of crops and the compound is applied at an application rate from 0.01 kg to 4.0 kg per hectare.

40 12. A method according to claim 10 in which the locus is an area which is not a crop-growing area and the compound is applied at an application rate from 1.0 kg to 20.0 kg per hectare.

13. A compound of formula (Ia) as defined in claim 5.

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